DEPARTMENT OF COMMERCE

BUREAU OF STANDARDS
WASHINGTON

Letter
Circular
LC 208

September 21, 1926

ZINC PLATING FROM ACID BATHS

I - Introduction[1]

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[1] Further details of this work are given in a paper to be presented at the Washington Meeting of the American Electrochemical Society, October 7-9, 1926 and to be published in Volume 50 of their Transactions.

Zinc plating or electrogalvanizing is so extensively used for protecting iron and steel against corrosion that little comment on its importance is needed. It was proposed in France as early as 1840, introduced in this country about 1890 and by 1905 was being used quite widely. Up to 1916, most commercial plating was confined to acid baths but at that time the alkaline cyanide bath also began to be used. In spite of the importance of acid zinc baths and the long experience with them, few extensive researches on the subject have been published, and it is safe to assume that practice has changed little during the last twenty years. It was hoped to conduct an extensive survey during the course of this investigation of acid zinc baths at this Bureau, but it was soon apparent that unusual difficulties prevented radical improvement of present methods. Only the most promising points, therefore, could be selected for preliminary study in the available time.

It is well known that acid zinc baths are characterized by poor throwing power and a tendency to produce coarsely crystalline deposits. To overcome the latter defect, numerous addition agents, usually organic, have been proposed for making the deposits smoother and brighter. There has been much less uniformity in composition of bath than in nickel or copper plating, perhaps because numerous formulas for zinc baths gave about the same result. It has been customary to use a high concentration of a zinc salt, sulfate or chloride, or both, together with a low concentration of a sodium, ammonium or magnesium salt to improve conductivity. As will be brought out subsequently, relatively high concentrations of the latter salts are required to produce a marked effect on conductivity.

II - Experimental

Acidity. As the acidity or pH has been found very important in nickel plating, its effect on zinc plating was studied first.

It was found that a pH range from 3.5 to 4.5 is suitable for securing high cathode current efficiency and good deposits which, just as with nickel, are somewhat finer grained when the pH is low. In this range, moreover, there is no excessive anode corrosion such as is caused by the chemical attack of more acid zinc solutions. The indicator, bromphenol blue, was found reliable for the control of pH.

Aluminum salts, such as alum or aluminum sulfate, have been much used in zinc baths. When these salts are present and the pH is raised, aluminum hydroxide begins to precipitate at a pH slightly above 4 and when 4.5 is reached only a small concentration of aluminum is left in solution. The precipitated aluminum hydroxide is readily redissolved by adding acid. In baths without aluminum salts, such as those containing acetates or boric acid, a higher pH may be used. The limiting pH is that at which zinc hydroxide itself precipitates, which has been shown by previous investigators to occur at about 6. This value, therefore, constitutes the upper limit for all simple acid zinc baths.

In order to maintain a definite pH, it is desirable to add a "buffer", which prevents any great change when a small amount of acid or alkali is added. Aluminum salts act as buffers through the formation of colloidal or precipitated aluminum hydroxide, or basic aluminum salts, and their re-solution. Acetates, citrates and tartrates all give a strong buffer effect but only the acetate solutions are stable. Neither ammonium salts nor boric acid have an appreciable buffer action in ordinary zinc baths.

III. Polarization and Throwing Power

Previous investigators have shown that throwing power depends essentially on three factors, cathode polarization, cathode current efficiency and conductivity, of which the first is usually the most important. As preliminary experiments showed that zinc solutions as a rule possess comparatively slight polarization, special efforts were made to improve this condition.

For a given current density and acidity, the usual methods of increasing polarization depend on: adding a common ion; increasing the solution viscosity; using an addition agent, usually an organic substance; or forming complex ions. The common ion effect, as produced by adding sodium sulfate to a zinc sulfate bath, or sodium or ammonium chloride to a zinc chloride bath, was found to be very small. These additions also increase the viscosity, which may be further raised by adding such substances as "corn sirup", or glycerin. When tried, however, it was found that both the latter failed to increase materially the useful polarization.

A few organic substances were also tried as addition agents, including dextrin, dextrose ("corn" or "grape" sugar), "corn sirup" (dextrin plus dextrose) and beta-naphthol. These experiments are not here reported in detail, as with the exception of dextrin, which slightly increased the polarization and produced much smoother and finer-grained (although darker) deposits, no very encouraging results were obtained. At low current densities, these additions seemed to have little effect on the natural tendency of zinc to deposit in isolated, coarsely-crystalline growths (furnishing slight protection to the base metal), while at high current densities they often tended to produce defects, such as pits, blisters or streaks and dark or spongy deposits. As it was possible to study the action of only a few of these substances in the available time and as this is a large field for investigation, no generalizations will be attempted. It is quite possible that other addition agents, used singly or in combination, might give better results than were here obtained.

Sodium citrate was tried for the complex ion effect, but no marked increase in useful polarization was found when it was used in the presence of inorganic salts, such as sulfates or chlorides. In alkaline zinc cyanide baths, which were outside the scope of the present research, zinc is, of course, present in complex ions. A few tests on a typical commercial cyanide bath, which were made merely for comparison, showed that the high throwing power of such baths is due chiefly to their high polarization.

Tests on a wide variety of acid zinc baths showed that the cathode current efficiency is very high (nearly 100 per cent) when the pH is 4 or above and the current density is above 5 amp./sq.ft. (0.5 amp./dm^2), although the efficiency decreases greatly at lower current densities.

The resistivity of acid zinc baths of the usual commercial type was found to be from about 15 to 25 ohm-cm at 25°C (77°F). A typical zinc cyanide bath has a resistivity of 7 ohm-cm.; nickel plating baths range from 9 (high sulfate) to 25 ohm-cm.; acid copper baths for electroplating or electrotyping range from 3 to 5 ohm-cm.

The throwing power of all the acid zinc baths tried was close to zero and was not greatly increased by any improvement in polarization, current efficiency or conductivity that could be effected.

IV. Baths of High Conductivity (Low Resistivity)

In view of these facts, the most promising way of improving the conditions in zinc deposition, other than throwing power, appeared to be by using more highly conducting baths. In such
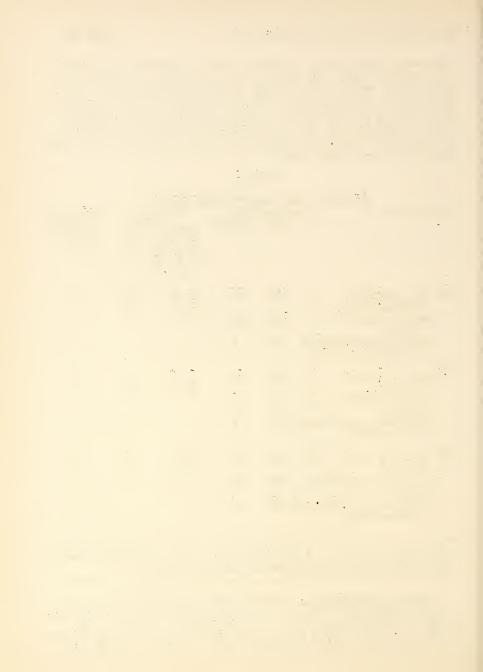
baths very high current densities can be applied which permit more rapid plating and produce better deposits. In electrodeposition, raising the average current density, up to a certain point, causes brighter and finer-grained deposits, while increasing the conductivity permits raising the average current density without causing roughness or treeing on sharp edges. Accordingly, the baths listed in Table 1 were devised and tried in extensive laboratory tests with results that justify their commercial trial.

Table 1

Proposed Acid Zinc Plating Baths

| Composition | Concentration | | | Throwing Power[1] | | Resistivity at 25°C (77°F) ohm-cm |
	N	g/L	oz/gal	Total Current on 2 dm² Amp.	T %	
(1) Zinc sulfate (ZnSO$_4$.7H$_2$O)	2	288	38	0.50	-2	8
				2.00	+1	
Sodium chloride (NaCl)	3	175	23			
Aluminum sulfate (Al$_2$(SO$_4$)$_3$.18H$_2$O)	0.25	28	4			
(2) Zinc chloride (ZnCl$_2$)	2	136	18	0.50	+3	5
				2.00	+2	
Sodium chloride (NaCl)	4	234	31			
Aluminum chloride (AlCl$_3$.6H$_2$O)	0.25	20	3			
(3) Zinc chloride (ZnCl$_2$)	2	136	18	0.50	+1	3
				2.00	+2	
Ammonium chloride (NH$_4$Cl)	4	214	29			
Aluminum chloride (AlCl$_3$.6H$_2$O)	0.25	20	3			

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[1] For total current on 2 dm² (31 sq.in.) in a throwing power box with 5/1 ratio and capacity of 6 L (1.6 gal.).

Operating Conditions. The favorable conditions of operation for these baths were found to include a pH of 3.5 to 4.5, ordinary temperature, and a cathode current density of 15 to 45 amp./sq.ft. (1.6 to 4.8 amp./dm²) on articles of fairly simple shape in still solutions. With sufficient motion of

cathode or in agitated solutions, up to 150 amp./sq.ft. (16 amp./dm^3) may be used in some cases. The anode current density may be the same, or higher. To deposit a zinc coating with an average thickness of 0.0006" (0.015 mm), such as is frequently used on articles subjected to moderate exposure, requires about 500 ampere-minutes per sq.ft. Therefore, at 100 amp./sq.ft. (10.8 amp./dm^3) this average thickness is produced in about 5 minutes. Dextrin in these baths, e.g. 4 oz./gal. (30 g/L) produces smoother deposits, but these are darker and the permissible current density is lowered.
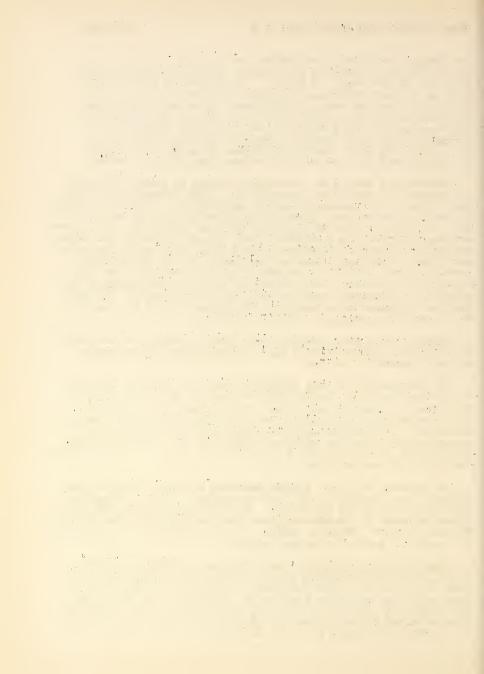
These baths should be especially useful in barrel plating on account of their high conductivity. The deposits from them were found to be unusually smooth and bright. Although aluminum has been at various times supposed to deposit as an alloy with zinc, none could be detected in these deposits. There are serious difficulties involved in depositing aluminum from aqueous solution and such deposition has never been satisfactorily confirmed. Besides aiding in regulating the pH and thereby preventing the pH of the cathode film from reaching too high a value, it is probable that colloidal aluminum hydroxide is of benefit in producing smoother and brighter deposits. The effect of aluminum salts upon both the solution and the deposit has been often mentioned by other authors.

Warming these baths would still further lower the resistivity (raise the conductivity) but is undesirable as it causes coarser-grained deposits.

The composition of the suggested baths is simple. Methods of chemical control merely involve measurement of pH and the titration of zinc and chloride. The content of the latter could probably be controlled approximately by specific gravity readings. Determinations of aluminum will be required only occasionally, likewise sulfate in Bath No. 1. The exact concentrations given in Table 1 are not essential and considerable variation is permissible.

In general, Bath No. 3 gave somewhat brighter deposits and changed less rapidly in pH than the others. It is, therefore, especially suggested for trial. As these baths have very low throwing power it is obvious that they are unsuited for plating objects of very irregular shape, at least unless it is feasible to resort to specially shaped anodes.

Possible Difficulties. One objection to "high chloride" baths, especially when agitated, is the increased tendency toward corrosion of copper bus bars. These may be protected to some extent by occasional greasing, or it may even be found preferable to substitute bus bars of aluminum. The latter are also attacked by chlorides but no new nor harmful constituent is thereby introduced into the solution.
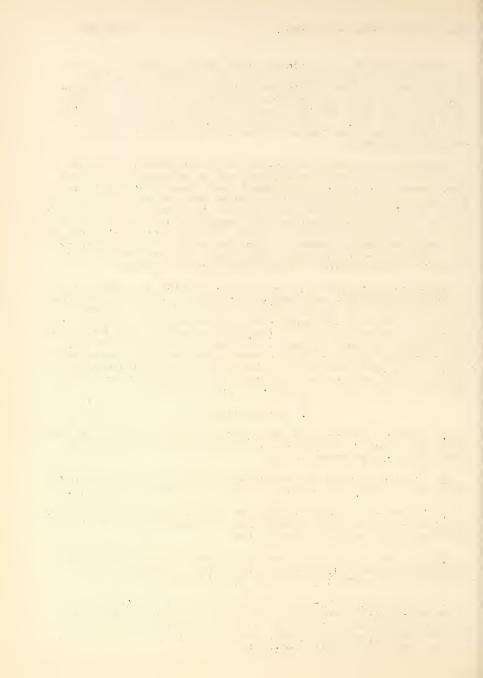
Another possible objection is the deteriorating effect of zinc chloride on wood tanks, which can, however, be sufficiently protected by bituminous linings. Still another objection that may arise is the increased solubility, in chloride solutions, of lead from low grade anodes, which might conceivably cause trouble. There is slight justification, however, for using other than the pure zinc anodes which are now so readily obtainable.

These baths are not very close to the saturation point of the salts at ordinary temperature, but an extreme temperature drop, especially if long continued, may cause precipitation. Any such precipitate should be readily redissolved on warming. It is desirable to prevent chilling of the baths in cold weather as the conductivity is materially sacrificed and likewise the permissible current density. Under some conditions dilution of the baths may be necessary. While the exact concentrations are not essential, as previously mentioned, dilution has the same effect on the operation as lowering the temperature.

Protective Value. The question may possibly arise with zinc coatings, as it has occasionally with nickel, of the protective value on steel when deposited from chloride baths. Recent tests have shown no inferiority of nickel deposits due to chloride in the solutions. It is difficult to settle this point for zinc without having available the results of long experience. Zinc chloride baths have been proposed and no doubt considerably used. A few preliminary salt spray and atmospheric exposure tests of zinc coatings of moderate thickness from these chloride baths have shown an entirely normal behavior.

V. Conclusions

1. Good results in zinc plating from acid baths are obtained in the range of pH 3.5 to 4.5, which can be controlled by the indicator, bromphenol blue.

2. Aluminum salts act as buffers and also cause whiter and brighter deposits, but without actual deposition of aluminum.

3. It was not found possible in these experiments to materially increase the throwing power of acid zinc baths, chiefly because of low cathode polarization.

4. No important results were obtained with the few organic addition agents tried, with the exception of dextrin, which produced finer-grained (although darker) deposits.

5. It was found that acid zinc baths could be distinctly improved by using very highly conducting solutions containing largely or entirely chlorides. In such solutions very high current densities can be used and very rapid plating conducted without producing treeing or roughness.

6. Excellent results were obtained with a bath containing 18 oz./gal. (136 g/L) zinc chloride, 31 oz./gal. (234 g/L) sodium chloride and 3 oz./gal. (20 g/L) aluminum chloride (crystallized) or 1.5 oz./gal. (11 g/L) aluminum chloride (anhydrous).

7. Preliminary observations indicate that zinc coatings of moderate thickness from such baths will furnish satisfactory protection against corrosion.